



Oxidative desulfurization of model diesel fuel catalyzed by carbon-supported heteropoly acids

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ABSTRACT

Keggin-type heteropoly acids supported on activated carbon (HPA/C) are active catalysts for oxidative desulfurization (ODS) of diesel fuel under mild conditions in a biphasic system composed of a benzothiophene-containing model diesel fuel (heptane) and aqueous 30% H_2O_2 . The catalytic activity of HPA/C was found to decrease in the order of HPA: $\text{H}_3\text{PMo}_{12}\text{O}_{40} > \text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40}$. The most active catalyst, $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{C}$, exhibited 100% removal of benzothiophenes from model diesel fuel at 60 °C, and could be recovered and reused without loss of activity. This catalyst outperforms other recently reported heterogeneous catalysts for ODS in similar systems. Kinetic and DRIFTS studies provide new insights into the mechanism of ODS reaction on carbon-supported HPAs.

1. Introduction

The sulfur content of diesel fuels used in transportation vehicles is under increasingly strict environmental regulations. It has decreased from 2000 to 10 ppm over the last 20 years and further reduction in sulfur content is desired [1,2]. Hydrodesulfurization (HDS), the most widely used technology for removing sulfur from diesel fuels, is operated at high temperature (300–400 °C) and pressure (30–130 atm) using alumina-supported Co-Mo or Ni-Mo catalysts [1,2]. The main drawbacks of HDS are severe operating conditions and low desulfurization efficiency in the case of refractory benzothiophenes. Alternative desulfurization methods have been investigated in recent years including, among others, oxidative desulfurization (ODS) [3,4], extraction [5], adsorption [6] and bio-desulfurization [7]. ODS appears to be the most promising method for deep desulfurization of diesel fuel. Typically, it involves liquid-phase biphasic oxidation of organosulfur compounds with H_2O_2 at low temperatures (50–70 °C) and atmospheric pressure to yield sulfoxides and sulfones, which can be separated from the fuel by precipitation, extraction or adsorption [3,4]. This method is highly efficient for removing refractory aromatic sulfur compounds such as thiols and benzothiophenes, which are difficult to remove by HDS [2].

Among many reported ODS catalysts, polyoxometalates (POMs), in particular Keggin-type POMs, exhibit a remarkable activity [8–13]. These compounds comprise polyanions, $\text{XM}_{12}\text{O}_{40}^{m-}$, composed of

oxygen-sharing MO_6 octahedra ($\text{M} = \text{Mo}^{\text{VI}}, \text{W}^{\text{VI}}, \text{V}^{\text{V}}, \text{etc.}$) encapsulating a central tetrahedron XO_4^{n-} ($\text{X} = \text{P}^{\text{V}}, \text{Si}^{\text{IV}}, \text{etc.}$) [13,42]. In solution, in the presence of hydrogen peroxide, these POMs degrade to form active peroxo-polyoxometalate species (peroxo-POM) [12,14,15], e.g., the Venturello peroxo complex, $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ [16]. Peroxo-POMs are highly active catalysts for various biphasic oxidations with hydrogen peroxide [17–20]. In these reactions, a phase transfer agent (PTA) is required to transfer the peroxo-POM species from the aqueous phase containing H_2O_2 to the substrate-containing organic or fuel phase. Most frequently, quaternary ammonium cations are used as the PTAs in such systems, including amino-modified high molecular weight alkene oligomers [20]. Alkylaminophosphazenes have also been reported as promising phase transfer agents in POM-catalyzed biphasic oxidations with H_2O_2 , including the oxidative desulfurization of benzothiophenes [12,21].

A major drawback of homogeneous POM catalysts in the PTA-assisted biphasic oxidative desulfurization is the difficulty of separating these catalysts from the fuel phase after desulfurization because the POM-PTA aggregates are highly soluble in the fuel phase. This would lead to contamination of fuel with POM. In this regard, heterogeneous ODS catalysts have the important advantage of easy catalyst separation from the fuel after reaction [22–28]. However, possible leaching of POM from the solid catalyst during the ODS reaction and post reaction catalyst treatment is a serious problem of the heterogeneous ODS systems. This may be addressed by incorporating POM within a metal-

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organic framework [26] or by chemical immobilization of POM onto an appropriately functionalized support [27]. A more practical solution to overcome this problem could be the use of porous supports that can strongly adsorb the active POM species.

This study aims at exploring activated carbon as a support for the heterogeneous ODS reaction catalyzed by POMs. Previously, it has been reported that activated carbon can strongly adsorb Keggin heteropoly acids (HPA), such as $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, irreversibly retaining 7–14 wt% of HPA in polar media such as water and methanol [29–31]. As a result, the corresponding HPA/C catalysts exhibit high stability towards HPA leaching in such media [30–32]. Strong interaction of HPA with carbon support is evidenced by a large line broadening in ^{31}P MAS NMR spectra of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on activated carbon [33]. From IR and ^{31}P MAS NMR, heteropoly acids $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ supported on a chemically (H_3PO_4) activated carbon retain the Keggin structure at an HPA loading > 5 wt% [33]. As evidenced by XRD, heteropoly acids form finely dispersed species on the carbon surface; no HPA crystal phase is developed even at a HPA loading as high as 45 wt% [33]. Microcalorimetry of ammonia adsorption shows that the acid strength of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is greatly reduced when loading on activated carbon [34,35]. This suggests HPA bonding through protonation of the carbon framework. Scanning tunnelling microscopy and tunnelling spectroscopy studies of HPA supported on graphite have been reported [36]. Carbon-supported POMs are well-documented catalysts for liquid-phase oxidation [37–39]. Recently, a polyoxometalate $[\text{PSPy}]_3\text{PMo}_{12}\text{O}_{40}$ supported on graphite, where PSPy is N -(3-sulfonatopropyl)-pyridinium ion, has been reported as an efficient ODS catalyst [28].

This work investigates heterogeneous catalysis by Keggin-type HPAs ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$) supported on activated carbon (HPA/C) for the biphasic oxidative desulfurization of model diesel fuel (heptane) by aqueous 30% H_2O_2 . We report a highly efficient catalyst, $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{C}$, for the oxidation of benzothiophenes (benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT)) to the corresponding sulfones by H_2O_2 . This catalyst shows a higher catalytic activity for the oxidation of benzothiophenes than other recently reported heterogeneous ODS catalysts in similar systems [22–27]. Strong adsorption of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ onto the carbon support stabilizes the HPA structure and prevents the HPA from leaching. In addition, our kinetic and infrared spectroscopic studies provide new insights into the mechanism of ODS reaction on carbon-supported HPAs.

2. Experimental

2.1. Chemicals

Benzothiophene (BT, 99%), dibenzothiophene (DBT, 99%), 4,6-dimethyldibenzothiophene (DMDBT, 97%), heptane (99%), dodecane (99%), 30% H_2O_2 , heteropoly acid hydrates $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (99%), $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (99.9%) and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (99.9%) containing 20–28 H_2O molecules per Keggin unit were all purchased from Sigma–Aldrich. Darco KB-B activated carbon wet powder (150 μm particle size) was also from Sigma–Aldrich. It contained < 100 ppm of Fe and 0.5% of extractable phosphates. From our thermogravimetric analysis (TGA), the activated carbon contained 17% of water (Supplementary Information, Fig. S1). Its elemental composition (%): C, 72.0; H, 3.0; N, 0.0; S, 0.0; O, 25.0 (by difference). Infrared spectrum of the activated carbon is shown in Fig. S2.

2.2. Catalyst preparation

The carbon-supported HPA catalysts (HPA/C) were prepared by impregnating Keggin-type heteropoly acids $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (HPMo), $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (HSiW) onto Darco KB-B activated carbon from aqueous solutions. The amount of crystallisation water in

Table 1

Information about HPA/C catalysts.

| Catalyst ^a | $S_{\text{BET}}^b \text{ m}^2 \text{ g}^{-1}$ | Pore volume ^c $\text{cm}^3 \text{ g}^{-1}$ | Pore diameter ^d Å |
|-----------------------|---|---|------------------------------|
| Activated carbon | 977 | 0.89 | 35 |
| 10.9%HPMo/C | 1072 | 0.94 | 34 |
| 11.0%HPW/C | 1006 | 0.85 | 33 |
| 12.7%HSiW/C | 1002 | 0.88 | 34 |

^a HPA loading calculated from Mo and W content determined by ICP-OES analysis.

^b BET surface area.

^c Single point pore volume.

^d Average pore diameter.

the commercial HPA hydrates was determined by TGA and taken into account in catalyst preparation. The HPA hydrates (0.15 g of anhydrous HPA) were placed in a 200-mL glass beaker and dissolved in a minimum amount of distilled water. Darco KB-B activated carbon (0.85 g) was added to the beaker and the mixture was magnetically stirred for 3 h at 40 °C. The beaker was then placed in an oven and the content was dried at 100 °C overnight to afford the catalysts as black powders. The HPA loading in the catalysts was in the range of 11–13 wt% as determined from Mo and W analysis by ICP-OES (inductively coupled plasma - optical emission spectrometry) after digesting catalyst samples in aqueous 15% KOH. From TGA, the catalysts thus prepared contained 8% of water (Fig. S3). The HPA/C catalysts were kept in a desiccator over calcined silica gel. The information about HPA/C catalysts is given in Table 1.

2.3. Techniques

BET (Brunauer-Emmett-Teller) analysis of catalyst samples was conducted on a Micromeritics ASAP 2010 instrument by measuring N_2 physisorption at -196°C . The samples were pre-treated at 220 °C under vacuum (1 Pa). DRIFT (diffuse reflectance infrared Fourier transform) spectra were recorded on a Nicolet Nexus FTIR spectrometer using powdered catalyst mixtures with KBr. The spectra were recorded at room temperature in the absorbance mode by averaging 254 scans in the range of 4000–500 cm^{-1} with a resolution of 4 cm^{-1} . DRIFT spectra of pure HPAs were measured against a KBr background and the spectra of HPA/C samples against a mixture of KBr and Darco KB-B activated carbon as the background. OMNIC software was used for data processing. Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer TGA-7 instrument. HPA loading in the catalysts was determined on a Spectro Ciros ICP-OES analyzer; the HPA/C samples were digested by boiling in aqueous 15% KOH.

2.4. Reaction procedure

The oxidation of benzothiophenes by 30% hydrogen peroxide in the presence of HPA/C catalysts (≤ 1 wt% per total reaction mixture) was carried in a two-phase system, heptane- H_2O , with a water content of ~2 vol.% added with aqueous 30% H_2O_2 . To a 50 mL jacketed glass reaction vessel equipped with a heat circulator, a magnetic stirrer and a reflux condenser were added, unless stated otherwise: HPA/C catalyst (0.0041 mmol of HPA), heptane (5.0 mL) and aqueous 30% H_2O_2 (1.5 mmol, the concentration of H_2O_2 was standardised by titration with KMnO_4). The reaction mixture was stirred at 60 °C for 5 min to activate the catalyst. The stirrer was stopped and 5.0 mL of heptane stock solution containing BT, DBT or DMDBT (0.50 mmol) and dodecane (0.40 mmol, GC internal standard) was added to the reaction mixture. The stirrer was then switched on to start the reaction. Catalyst pre-activation at the reaction temperature (60 °C/5 min) prior to adding the substrate allowed to exclude any induction period that otherwise could have taken place [27]. Typically, the reaction was carried out at 60 °C and 1500 rpm stirring speed unless stated otherwise. Reaction

rate did not depend on the stirring speed in the range of 500–1500 rpm (Fig. S4), which indicates no external diffusion limitation. The conversion of benzothiophenes was monitored by submitting aliquots of the organic phase (0.1 mL, centrifuged to separate the catalyst) for analysis by gas chromatography (GC) using the internal standard method (a Varian Chrompack CP-3380 gas chromatograph equipped with a flame ionization detector and a $25\text{ m} \times 0.32\text{ mm} \times 0.5\text{ }\mu\text{m}$ BP1 capillary column). The mean absolute percentage error in substrate conversion was $\leq 5\%$. The reaction products, benzothiophene sulfones, were not soluble in heptane and precipitated from the reaction mixture. To determine the sulfone yield, after the ODS reaction had reached completion, the reaction mixture was diluted with 1,2-dichloroethane, stirred at $60\text{ }^{\circ}\text{C}$ for 5 min to dissolve the sulfones and analyzed using GC.

For catalyst reuse in DBT oxidation, the initial reaction was run using the above procedure for 1 h. After the reaction had reached completion, the catalyst was separated and washed with toluene and then with heptane using a centrifuge. Afterwards, the catalyst was returned to the reactor along with the required amounts of all other reaction components (30% H_2O_2 , dodecane, DBT and heptane) for the next run.

3. Results and discussion

3.1. Catalyst characterization

The carbon-supported HPA catalysts were prepared using a simple wet impregnation procedure with HPA loading in the range of 11–13 wt % (Table 1). The HPA loading did not change after stirring the catalysts (0.5 g) in water (100 mL) at $60\text{ }^{\circ}\text{C}$ for 1 h. This confirms the strong adsorption of HPAs onto the carbon surface, in agreement with previous reports [29–31], and ensures stability of the HPA/C catalysts toward HPA leaching during the ODS process.

The loading of HPAs onto activated carbon had a very little effect on the microporous texture of the support, as evident from the nitrogen adsorption/desorption isotherms shown in Fig. 1 for HPMo/C and Figs. S5–S8 for HPW/C and HSiW/C. It increased the surface area only slightly (3–10%), with the pore volume and pore diameter remaining practically unchanged (Table 1). This indicates that the HPA was mostly present on the outer surface rather than occupying the pores of carbon support.

As evidenced by DRIFT spectroscopy, despite strong HPA-support interaction, the HPAs retained the Keggin structure upon their loading onto the carbon support. For the HPMo catalyst, this is clearly seen in Fig. 2, which shows the DRIFT spectra for the fresh HPMo/C catalyst (spectrum 2) and bulk crystalline HPMo (spectrum 1) as a reference; the latter shows the four characteristic bands at 1062 cm^{-1} (P–O), 960 cm^{-1} (Mo=O), 884 cm^{-1} (Mo–O–Mo corner-sharing) and 811 cm^{-1} (Mo–O–Mo edge-sharing), in agreement with the literature

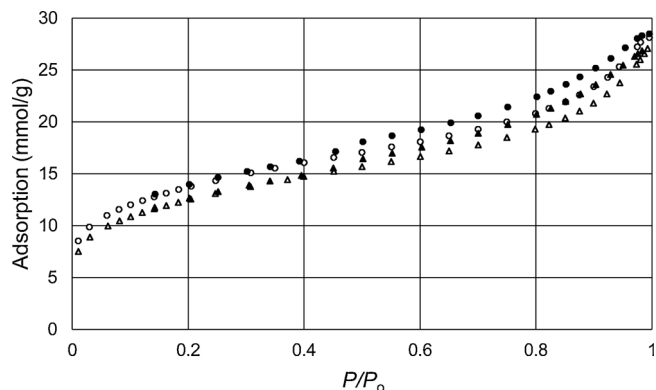


Fig. 1. Nitrogen adsorption (solid markers) and desorption (open markers) for Darco KB-B activated carbon (triangles) and 10.9%HPMo/C catalyst (circles).

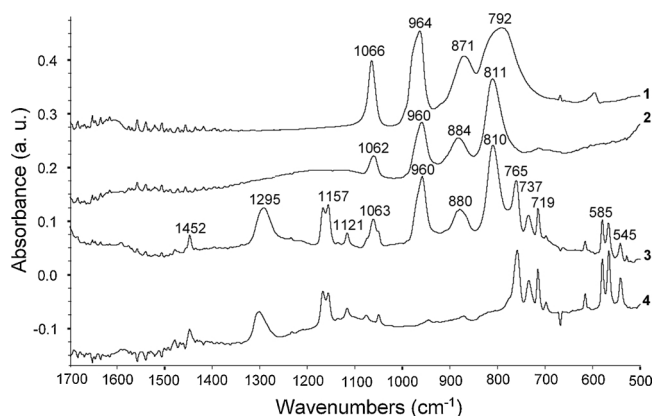


Fig. 2. DRIFT spectra of (1) bulk $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, (2) fresh 10.9%HPMo/C catalyst, (3) spent 10.9%HPMo/C catalyst after 8 successive runs of DBT oxidation and (4) DBT sulfone adsorbed on activated carbon (powdered sample mixtures with KBr; (1) versus pure KBr background, (2) – (4) versus a mixed KBr + carbon background).

[40]. Close resemblance between the two spectra confirms the integrity of the Keggin structure in the carbon-supported HPMo. The same conclusion also applies to HPW/C and HSiW/C catalysts (their DRIFT spectra are presented in Figs. S9 and S10, respectively), in agreement with previous report [33].

It should be noted that there is a small ($10\text{--}20\text{ cm}^{-1}$) blue shift of the edge-sharing M–O–M band in HPA/C catalysts in comparison to the corresponding bulk HPAs (Fig. 2, Figs. S9 and Fig. S10). This may be explained by protonation of the edge-sharing bridging oxygens in supported HPAs. It is well known that protons in the HPA crystal lattice link the neighboring polyanions through the oxygen atoms of the terminal M=O groups, as evidenced by single-crystal X-ray and neutron diffraction data for HPW hexahydrate [41]. On the carbon surface, however, no HPA crystal phase has been found even at HPA loadings as high as 45 wt% [33]; in this case, the HPA would rather exist as a molecular dispersion. In isolated HPA molecules, in contrast to the crystalline HPA, protons are likely to be localized on the edge-sharing bridging oxygens that have a larger negative charge [13,42].

3.2. Oxidation of benzothiophenes by H_2O_2 catalyzed by HPA/C

The HPA/C catalysts comprising Keggin-type HPAs (HPMo, HPW and HSiW) supported onto activated carbon were used for ODS reaction in a biphasic heptane– H_2O (98:2 v/v) system, with heptane as a model diesel fuel and benzothiophene (BT, DBT or DMBT, 1 wt%) as an organosulfur compound. 30% H_2O_2 was used as an oxidant; unless otherwise stated, it was used in 50% excess to the stoichiometric amount to ensure 100% conversion of benzothiophenes. Most of the work was carried out with DBT because the oxidation of DBT is typically employed as a model reaction for testing desulfurization catalysts, hence making it easier to compare catalyst performance of different catalyst systems in the literature.

Representative results are given in Table 2. The catalytic activity of HPAs in the oxidation of DBT was found to decrease in the order $\text{HPMo} > \text{HPW} > \text{HSiW}$ (entries 1–3 in Table 2, Fig. 3). The same activity trend has been found previously in biphasic systems with homogeneous [12] and heterogeneous [27] POM catalysts modified with alkylaminocyclophosphazenes. Under our conditions, with H_2O_2 added in 50% excess, the oxidation of DBT gave DBT sulfone as the final product in a $100 \pm 13\%$ yield (determined by GC analysis), with only traces of DBT sulfoxide found. Therefore, the oxidation of DBT can be represented by Scheme 1.

Activated carbon is well known to adsorb benzothiophenes from hydrocarbon media, and this has been used for desulfurization of diesel fuel [6]. In our system, however, this played only a minor role as only

Table 2Oxidation of benzothiophenes by H₂O₂ in heptane-H₂O (98:2 v/v) system using HPA/C catalysts.^a

| Entry | HPA/C | Substrate | H ₂ O ₂ /S ^b mol/mol | Time h | Conversion ^c % |
|-------|-------------------------------|-----------|---|--------|---------------------------|
| 1 | 10.9%HPMo/C | DBT | 3.0 | 0.5 | 100 ^d |
| 2 | 11.0%HPW/C | DBT | 3.0 | 3.0 | 89 |
| 3 | 12.7%HSiW/C | DBT | 3.0 | 3.0 | 49 |
| 4 | 10.9%HPMo/C | DBT | 2.0 | 1.5 | 98 ± 2 ^e |
| 5 | 10.9%HPMo/C | DBT | 0 ^f | 3.0 | 5 ^g |
| 6 | Activated carbon ^h | DBT | 3.0 | 3.0 | 30 |
| 7 | 10.9%HPMo/C | BT | 3.0 | 2.0 | 100 ⁱ |
| 8 | 10.9%HPMo/C | DMDBT | 3.0 | 1.0 | 100 ^d |

^a 60 °C, HPA (0.0041 mmol), substrate (BT, DBT or DMDBT, 0.50 mmol), H₂O₂ (1.50 mmol, 0.166 mL of 30% H₂O₂ (9.05 M) unless stated otherwise), dodecane (GC standard, 0.40 mmol) and heptane (10 mL); stirring speed 1500 rpm.

^b H₂O₂/substrate molar ratio.

^c Substrate conversion to sulfone.

^d 80% H₂O₂ efficiency from post reaction titration with KMnO₄; the yield of DBT sulfone 100 ± 13%.

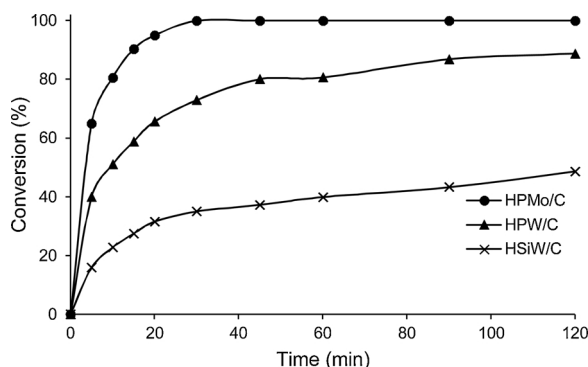
^e Reaction at stoichiometric molar ratio H₂O₂/S = 2.0; hydrogen peroxide efficiency 98 ± 2% (average of three runs).

^f 0.2 mL H₂O added instead of 30% H₂O₂.

^g The percentage of DBT adsorbed on the catalysts.

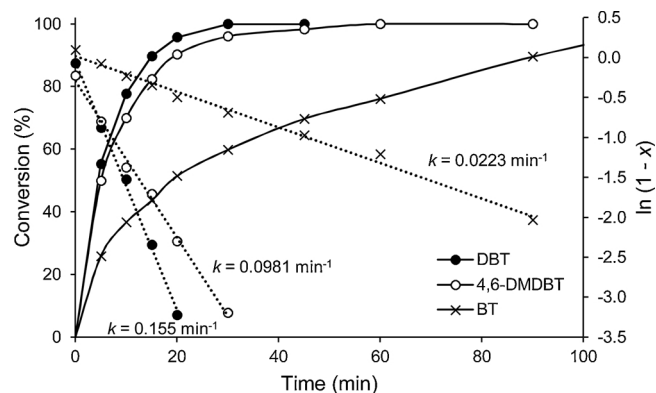
^h 0.024 g of activated carbon added instead of HPA/C catalyst.

ⁱ ≥ 75% H₂O₂ efficiency.

**Fig. 3.** Effect of HPA on the oxidation of DBT (0.50 mmol) by H₂O₂ (1.5 mmol) in heptane (10 mL) catalyzed by HPA/C at 60 °C (HPA, 0.0041 mmol).

5% of DBT was adsorbed on the HPMo/C catalyst in the absence of H₂O₂ (Table 2, entry 5). Also, activated carbon itself has been reported to catalyze the oxidation of DBT by H₂O₂ [43]. This was found to take place in our system as well, contributing up to 30% of DBT conversion (Table 5, entry 6). No reaction between DBT and H₂O₂ was observed in a blank test at 60 °C in the absence of catalyst and neat carbon support.

The reactivity of benzothiophenes was found to decrease in the order DBT > DMDBT > BT (Table 2, entries 1, 7 and 8; Fig. 4). The same trend has also been observed in homogeneous and other heterogeneous ODS systems [3,4,8,9,12,28,44,45]. It can be attributed to the electron density on the S atom and steric effects of the methyl groups in DMDBT [9]. The electron density on the S atom increases in the order BT < DBT ≈ DMDBT, which can explain the lower reactivity of BT as compared to DBT and DMDBT. On the other hand, the S atom in DMDBT is sterically hindered by the two neighboring methyl groups

**Fig. 4.** Plot of substrate conversion (x) versus reaction time and first-order plot $\ln(1-x) = -kt$ for oxidation of BT, DBT and 4,6-DMDBT (0.50 mmol) by H₂O₂ (1.5 mmol) in heptane (10 mL) catalyzed by 10.9%HPMo/C (0.0685 g, 1.0 wt%, 0.0041 mmol HPMo) at 60 °C.

rendering it less reactive compared to DBT [9].

The efficiency of ODS depended on the relative amount of H₂O₂ in the reaction mixture, increasing with an increase in the H₂O₂/DBT molar ratio. Increasing the amount of H₂O₂, however, led to a decrease of the reaction selectivity based on H₂O₂ (H₂O₂ efficiency) due to non-productive decomposition of H₂O₂ to form O₂ and H₂O. For the HPMo/C catalyst, an optimum H₂O₂/DBT molar ratio was found to be 3.0 (50% H₂O₂ excess), which gave a 100% DBT conversion at 60 °C in 0.5 h with an 80% H₂O₂ efficiency as determined by post reaction titration with KMnO₄ (Table 2). At stoichiometric ratio H₂O₂/DBT = 2.0 and otherwise the same conditions, the reaction reached a maximum 98% conversion in 1.5 h, thus providing 98% H₂O₂ efficiency (Table 2, entry 4). The decrease in H₂O₂ efficiency with increasing the concentration of H₂O₂ could be the result of zero order of the ODS reaction in H₂O₂ (see below) and a positive order of the non-productive H₂O₂ decomposition in H₂O₂. The H₂O₂ efficiency was also found to decrease with increasing the reaction temperature above 60 °C due to a faster decomposition of H₂O₂.

Notably, the HPMo/C catalyst was found to be more active than its recently reported homogeneous analogue with hexylaminocyclophosphazene (HexPN) as a phase transfer agent [12]. The HPMo/C catalyst gave 100% DBT conversion in 0.5 h at 60 °C (Table 2), whereas PMo-HexPN gave only 79% conversion under the same reaction conditions and with the same HPMo loading [12]. This may be explained by adsorption of DBT onto the surface of carbon support, which could increase the local concentration of DBT in the vicinity of active catalyst sites.

The HPMo/C catalyst showed higher activity than other heterogeneous catalysts that have been reported recently for the oxidation of DBT with hydrogen peroxide in similar systems [24–28]. Unfortunately, the data on turnover reaction rates are limited in the literature. Therefore, the results from different reports are compared on the basis of DBT conversion focusing on parameters such as H₂O₂/DBT molar ratio, reaction temperature and reaction time (Table 3). Ti(IV) grafted onto silica gives 99% DBT conversion to sulfone in isooctane with 10–60% H₂O₂ at 60 °C in 8 h reaction time [24]. With hybrid catalysts comprising Zr(IV) and Hf(IV) oxoclusters in poly(methylmethacrylate) matrix, 84% DBT conversion to sulfone with 94% selectivity has been obtained in octane with 30% H₂O₂ at 65 °C in 24 h [25]. A

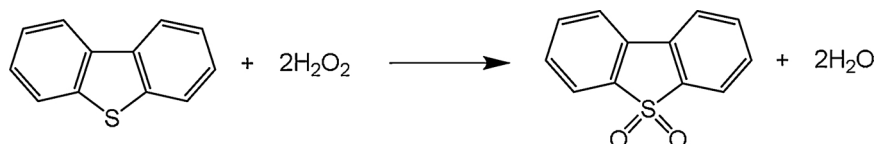
**Scheme 1.** Oxidation of DBT to sulfone by H₂O₂.

Table 3Comparison of heterogeneous catalysts for oxidation of DBT by H₂O₂ in model diesel fuel^a.

| Catalyst | Model diesel | H ₂ O ₂ /DBT mol/mol | T °C | Time h | DBT conversion % | Reference |
|--|--------------|--|------|--------|------------------|-----------|
| HPMo/C | heptane | 3.0 | 60 | 0.5 | 100 | This work |
| Ti(IV)/SiO ₂ | isooctane | 5.0 | 60 | 8 | 99 | [22] |
| Zr(IV)/PMMA ^b | octane | 3.5 | 65 | 24 | 84 | [23] |
| PW ₁₁ Zn-MOF ^c | octane | 50 | 50 | 6 | 100 | [24] |
| PMo/BzPN-SiO ₂ ^d | heptane | 3.0 | 60 | 3 | 100 | [25] |
| [PSPy]PMo/C ^e | octane | 3.0 | 50 | 1 | 100 | [26] |

^a Biphasic systems comprising a model diesel phase and aqueous H₂O₂ phase.^b Zr(IV) oxoclusters in poly(methylmethacrylate) matrix (PMMA).^c MOF comprising PW₁₁Zn polyoxometalate and 2-aminoterephthalic acid in octane–[BIMIM]PF₆ biphasic system.^d PMo polyoxometalate immobilized on phosphazene-functionalized silica.^e 5%[PSPy]₃PMo₁₂O₄₀/Graphite (PSPy = N-(3-sulfonatopropyl)-pyridinium ion), 1% in reaction mixture.

polyoxometalate-MOF composite comprising PW₁₁Zn and 2-aminoterephthalic acid in octane–[BIMIM]PF₆ biphasic system at 50 °C gives 70% DBT conversion in 4 h and 100% in 6 h reaction time; however this has been obtained using a 50-fold molar excess of H₂O₂ over DBT [26]. In this system, the ionic liquid [BIMIM]PF₆ is used to extract the product sulfone from the model diesel. Keggin PMo polyoxometalate immobilized on phosphazene-modified silica PMo/BzPN-SiO₂ gives 100% DBT conversion in heptane with 30% H₂O₂ at H₂O₂/DBT = 3.0 and 60 °C, but it takes a longer reaction time of 3 h [27]. 5%[PSPy]₃PMo₁₂O₄₀/Graphite catalyst (1 wt% in fuel), where PSPy is N-(3-sulfonatopropyl)-pyridinium ion, gives 100% DBT conversion at 50 °C, H₂O₂/DBT = 3.0 and 1 h reaction time [28], which is close to the performance of our 10.9%HPMo/C catalyst (1 wt% in fuel, H₂O₂/DBT = 3.0, 60 °C, 0.5 h). However, the 5%[PSPy]₃PMo₁₂O₄₀/Graphite catalyst is prepared by a tedious and lengthy hydrothermal procedure [28], whereas our catalyst is easily obtained from off-the-shelf components by a straightforward wet impregnation procedure (Sect. 2.2).

Moreover, the HPMo/C catalyst exhibited excellent recyclability; it was reused eight times in the oxidation of DBT at 60 °C, giving 100% DBT conversion after each use (Fig. 5). After eight catalyst recycles, catalyst productivity amounted to 10 g DBT per 1 g catalyst and 94 g DBT per 1 g HPMo. The successful catalyst reuse indicates no leaching of HPMo from the catalyst. The lack of leaching is further supported by ICP-OES analysis, which found no Mo in aqueous extract from the reaction mixture after reaction, thus supporting true heterogeneous catalysis in the ODS reaction.

3.3. Kinetics and mechanism

Further kinetic and DRIFT spectroscopic studies provided an important insight into the mechanism of the ODS reaction catalyzed by carbon-supported HPA.

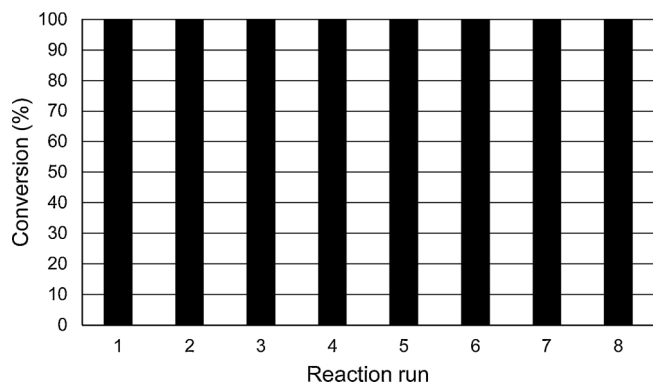


Fig. 5. Catalyst reuse in oxidation of DBT (0.50 mmol, 1.3 wt% in reaction mixture) by H₂O₂ (1.5 mmol) in heptane (10 mL) catalyzed by 10.9%HPMo/C (0.0685 g, 1.0 wt%, 0.0041 mmol HPMo) at 60 °C, 1 h.

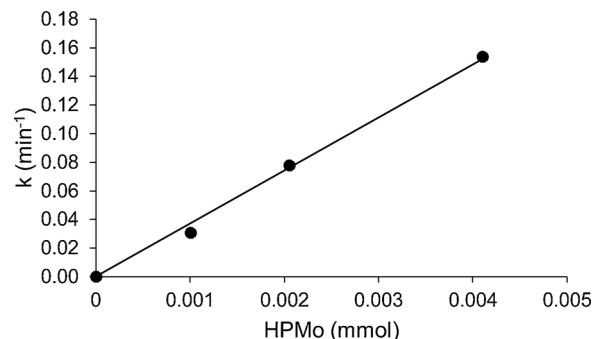


Fig. 6. Arrhenius plot for oxidation of DBT (0.50 mmol) by H₂O₂ (1.5 mmol) catalyzed by 10.9%HPMo/C (0.0343 g, 0.0020 mmol HPMo).

As expected, the rate of ODS reaction increased with increasing the temperature. For the oxidation of DBT with HPMo/C catalyst, the apparent activation energy was found to be 49 kJ mol⁻¹ in the temperature range 40–70 °C (the Arrhenius plot is shown in Fig. 6). This value is high enough to indicate the absence of diffusion limitations in the reaction system, which is also supported by the independence of reaction rate from the stirring speed (Fig. S4).

The oxidation of BT, DBT and DMBT in the presence of HPMo/C catalyst was found to be first order in benzothiophene (Fig. 4), with the rate constants 0.0223 ± 0.0008 , 0.155 ± 0.004 and 0.0981 ± 0.0031 min⁻¹, respectively, at 60 °C and other conditions specified in Fig. 4. The reaction was also found to be first order in the catalyst HPMo/C (Fig. 7). Therefore, the ODS reaction in the presence of HPMo/C obeyed the rate Eq. (1), where k_{ODS} is the second-order rate constant. The first order in benzothiophenes has also been reported for the ODS in the presence of [PSPy]₃PMo₁₂O₄₀/Graphite [28].

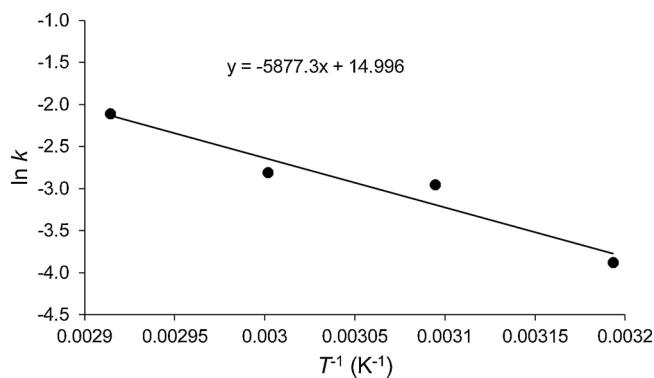


Fig. 7. Effect of catalyst amount on the rate of DBT (0.50 mmol) oxidation by H₂O₂ (1.5 mmol) catalyzed by 10.9%HPMo/C at 60 °C (k is the first-order rate constant).

$$-\frac{d[\text{DBT}]}{dt} = k_{\text{ODS}}[\text{HPMo}][\text{DBT}] \quad (1)$$

The first order reaction kinetics up to over 90% DBT conversion (Fig. 4) together with eight successive catalyst recycles at 100% DBT conversion each (Fig. 5) evidence against any significant catalyst deactivation during the ODS reaction.

It was found that a 4-fold decrease in concentration of H_2O_2 in the aqueous phase of the heptane- H_2O system did not affect the rate of DBT oxidation, which indicates zero reaction order in H_2O_2 . This was monitored by changing the heptane/ H_2O ratio from 98/2 to 93/7 v/v by adding 0.2–0.6 mL of H_2O to 10 mL of heptane at a constant amount of H_2O_2 (1.5 mmol) (Table S1).

Fig. 2 shows the DRIFT spectrum for the spent HPMo/C catalyst (spectrum 3) after eight successive runs presented in Fig. 5. Comparison with the spectrum of the fresh catalyst discussed above (spectrum 2) clearly shows that the spent catalyst retained the HPMo Keggin structure. Also the spent catalyst has some DBT sulfone adsorbed on its surface, as evident from comparison with the reference spectrum of the sulfone adsorbed on activated carbon (spectrum 4). This sulfone, however, did not affect catalyst activity as can be seen from the excellent catalyst reuse (Fig. 5).

Another important piece of evidence regarding the active state of HPA/C catalysts in the ODS system was obtained from DRIFT spectra of catalyst samples pretreated with H_2O_2 (Fig. 8 and Fig. S11). Generally, ^{31}P NMR is a very effective tool for such analysis [12,14,15]. But carbon-supported HPAs give broad ^{31}P MAS NMR peaks [33]; DRIFTS can provide more detailed information in this case. The catalysts were treated with 30% H_2O_2 under conditions similar to those used for the ODS reaction, except in the absence of benzothiophenes. HPMo/C and HPW/C samples (0.1 g) were stirred with 30% H_2O_2 (1.5 mmol) in heptane (5 mL) at room temperature or 60 °C for 10 min, filtered off using a Buchner funnel and dried under vacuum to afford a dry, black powder. The samples were ground with KBr, and their DRIFT spectra were measured against a mixture of KBr and activated carbon as the background. As seen in Fig. 8, the HPMo/C catalyst treated with H_2O_2 at room temperature as well as at 60 °C has exactly the same infrared spectrum as the fresh HPMo/C catalyst in the range of 700–1100 cm^{-1} , characteristic of the Keggin structure. This clearly shows that the structure remains intact after the H_2O_2 treatment. The same result was obtained for HPW/C catalyst (Fig. S11).

Overall, our DRIFTS data provide an important insight into the mechanism of ODS reaction over carbon-supported HPA catalysts, specifically regarding the active peroxo species involved in this

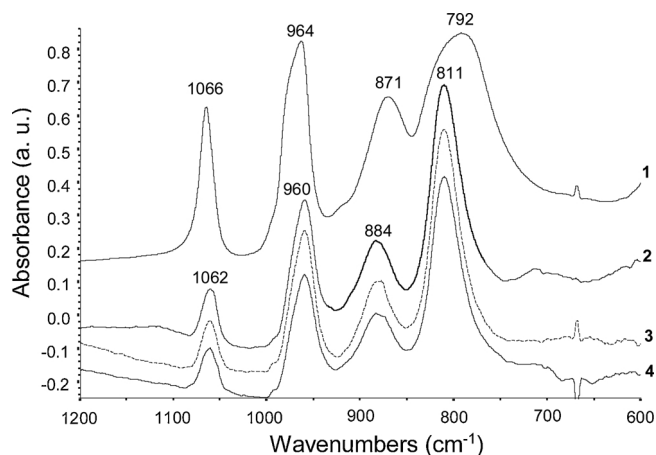
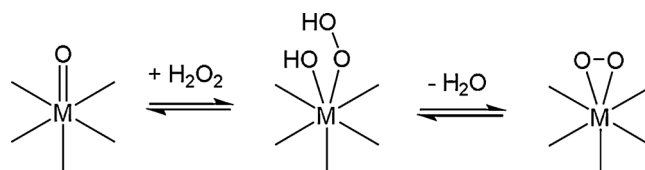
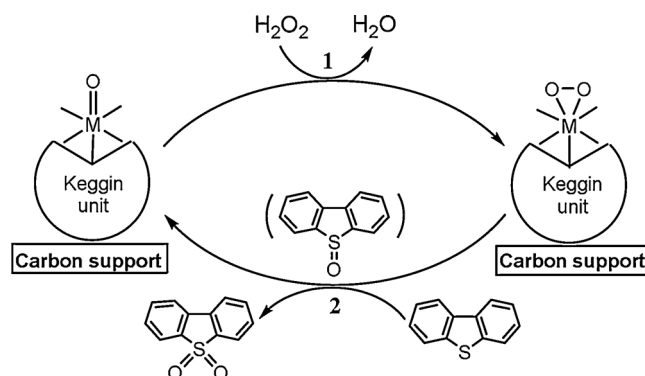


Fig. 8. DRIFT spectra of (1) bulk $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, (2) fresh 10.9%HPMo/C catalyst, (3) 10.9%HPMo/C catalyst treated with H_2O_2 at 60 °C and (4) 10.9%HPMo/C catalyst treated with H_2O_2 at 20 °C (powdered sample mixtures with KBr; (1) versus pure KBr background, (2) – (4) versus a mixed KBr + carbon background).



Scheme 2. Formation of peroxo moiety in metal-oxygen octahedron within Keggin HPA supported on activated carbon ($\text{M} = \text{Mo}^{\text{VI}}$ or W^{VI}).

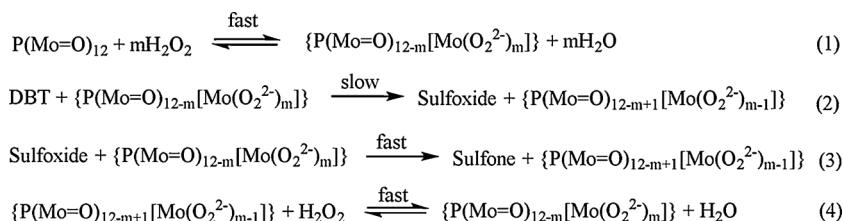


Scheme 3. Reaction scheme for oxidation of DBT by H_2O_2 catalyzed by HPA/C ($\text{M} = \text{Mo}^{\text{VI}}$ or W^{VI}).

reaction. It is evident that there is a clear difference between homogeneous and heterogeneous ODS based on the H_2O_2 /POM redox system. In homogeneous ODS and alkene epoxidation systems (including truly homogeneous as well as biphasic systems), it has been demonstrated that interaction between the Keggin POM and H_2O_2 leads to Keggin structure breakdown to form peroxo complexes (observed by ^{31}P and ^{183}W NMR), which act as the active oxidizing species in these reactions ([12,14,15] and references therein). Conversely, in the carbon-supported HPA catalysts, the Keggin structure is preserved due to strong interaction between molecularly dispersed HPA and the carbon surface. In this case, the active oxidizing species could be transient peroxo complexes formed between the intact Keggin polyanions and H_2O_2 .

The vast chemistry of peroxo complexes of $\text{Mo}(\text{VI})$ and $\text{W}(\text{VI})$, including general patterns of their structure and reactivity, has been thoroughly reviewed by Dickman and Pope [46]. It is recognized that the $\eta^2\text{-O}_2^{2-}$ peroxo ligand is a π -donor like the oxo ligand [46], and the terminal metal-oxo groups $\text{M}=\text{O}$ can be converted into η^2 -peroxo groups $\text{M}(\text{O}_2)^{2-}$. Thus the terminal bonds $\text{W}^{\text{VI}}=\text{O}$ converted into η^2 -peroxo groups $\text{W}^{\text{VI}}(\text{O}_2)^{2-}$ have been found in the lacunary Keggin polyanion $[(\text{Co}^{\text{II}}\text{O}_4)\text{W}_{11}\text{O}_{31}(\text{O}_2)_4]^{10-}$ [46]. It may therefore be suggested that the terminal $\text{Mo}=\text{O}$ and $\text{W}=\text{O}$ bonds in the Keggin HPMo and HPW can interact reversibly with H_2O_2 to form the corresponding labile η^2 -peroxo complexes without breaking the Keggin structure on the carbon surface, as shown in Scheme 2. These complexes can then act as the active oxidizing species in ODS reaction. Strong HPA adsorption on the carbon support is thought to be the key to high stability of the Keggin unit in the presence of H_2O_2 . It may not be the case with less adsorbing supports and weaker POM frameworks. Thus, the lacunary $[\text{PW}_{11}\text{O}_{39}]^{7-}$ unit within a solid hybrid catalyst has been reported to decompose upon interaction with H_2O_2 to form peroxo W^{VI} species [47].

The proposed reaction scheme for the oxidation of DBT in model diesel fuel by H_2O_2 catalyzed by HPA/C is shown in Scheme 3. In the initial step (1), the HPA reacts with H_2O_2 to form the peroxo species on the carbon surface. This species then oxidizes DBT to form DBT sulfone and the initial oxo species via step (2), thus completing the catalytic cycle. DBT sulfoxide may be formed in step (2), but probably does not desorb, being readily oxidized to DBT sulfone on the catalyst surface. In heptane- H_2O system, it was not possible to monitor the sulfoxide and



Scheme 4. Proposed step-by-step mechanism for DBT oxidation catalyzed by HPMo/C.

sulfone during reaction because neither was soluble; however intermediate formation of DBT sulfoxide has been observed in different solvents [48]. Sulfur-free diesel fuel can be separated from the solid catalyst and precipitated sulfone by filtration. The sulfone can be separated from the catalyst by solvent extraction (e.g., with toluene), and the catalyst can be reused.

Reflecting on the kinetic and DRIFTS results, the mechanism of oxidation of DBT catalyzed by HPMo/C may be represented by Scheme 4. In step (1), P(Mo=O)_{12} , the initial HPMo/C catalyst, reacts with hydrogen peroxide to form the peroxo species $\{\text{P(Mo=O)}_{12-\text{m}}[\text{Mo(O}_2^{2-})_{\text{m}}]\}$ as shown above in Scheme 2. From the DRIFTS results, the Keggin structure remains intact in the presence of H_2O_2 , which indicates that this peroxo species is labile and step (1) is probably equilibrated. This is followed by the oxidation of DBT to sulfoxide (step 2) and further to sulfone (step 3) by the peroxo species. As only traces of sulfoxide were found in the reaction products, it can be suggested that the oxidation of DBT to sulfoxide is the rate limiting step followed by fast oxidation of the sulfoxide adsorbed on the catalyst surface to sulfone. It has been reported that the sulfoxide is oxidised faster than DBT [49]. Finally, the active peroxo species is rapidly regenerated in step (4). Fast formation of the peroxo species in step (1) and its fast regeneration in step (4) will keep the concentration of the peroxo species constant as long as the amount of H_2O_2 in the reaction mixture exceeds the amount of HPMo. Consequently, as long as this stands, the ODS reaction will be first order in DBT and zero order in H_2O_2 . This is indeed the case as can be seen from the data in Fig. 4 and Table S1.

The order of HPA catalytic activity in the ODS reaction, $\text{HPMo} > \text{HPW} > \text{HSiW}$, is directly correlated with the rate of oxygen (^{17}O) exchange of Keggin heteropoly anions in aqueous solution, which increases in the order of addenda atoms $\text{W(VI)} < \text{Mo(VI)}$, as determined from ^{17}O NMR [50]. This is in agreement with the proposed mechanism via steps (1) – (4) because all these steps involve oxygen atom transfer to and from the addenda atoms, which can be expected to be more feasible for Mo(VI) than W(VI).

4. Conclusions

This work demonstrates that Keggin-type heteropoly acids supported on activated carbon are active catalysts for oxidative desulfurization (ODS) of model diesel fuel in a biphasic heptane- H_2O system using 30% H_2O_2 as an oxidant. The carbon-supported HPA catalysts are easily obtained from off-the-shelf components by a straightforward wet impregnation procedure. The catalytic activity of HPA/C decreases in the order of HPA: $\text{H}_3\text{PMo}_{12}\text{O}_{40} > \text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40}$. The most active catalyst, $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{C}$, removes 100% of benzothiophenes from model diesel fuel at 60 °C and could be recovered and reused many times without loss of activity. This catalyst outperforms other recently reported heterogeneous catalysts for ODS in similar systems. Kinetic and DRIFTS studies suggest a mechanism for heterogeneous ODS reaction on carbon-supported HPAs, which is different from that for a homogeneously-catalyzed ODS reaction. Carbon-supported HPAs, in contrast to their homogeneous counterparts, retain their Keggin structure and form labile active peroxo species without destruction of the HPA Keggin unit, which oxidize benzothiophenes to the corresponding sulfoxides and sulfones.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.04.063>.

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